



A new insight into the photocatalytic reduction of 4-nitroaniline to *p*-phenylenediamine in the presence of alcohols

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ABSTRACT

Photoreduction of 4-nitroaniline to *p*-phenylenediamine over TiO_2 , ZnO, $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and CdS photocatalysts in the presence of CH_3OH was investigated under light irradiation ($h\nu \geq \text{band gap}$) upon purging with N_2 . Compared with $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and CdS, TiO_2 and ZnO showed photocatalytic activities for the photoreduction of 4-nitroaniline. Electron spin resonance analysis results revealed that a methanol radical could be detected in the presence of TiO_2 and ZnO. Its formation was attributed to the reaction between the hydroxyl radical and CH_3OH molecule. The species had strong reductive ability, and therefore could reduce 4-nitroaniline to *p*-phenylenediamine. Other alcohols ($\text{C}_2\text{H}_5\text{OH}$ and *i*- $\text{C}_3\text{H}_7\text{OH}$) were also found to be efficient additives for the photoreduction of 4-nitroaniline. The results of the ^2H -labeled experiments indicated that the *p*-phenylenediamine formation was formed by the hydrogen transfer reaction between the 4-nitroaniline and H_2O molecules. A mechanism was proposed to explain the photoreduction of 4-nitroaniline to *p*-phenylenediamine in the present alcohols.

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1. Introduction

Organic synthesis by using photocatalysis (such as photocatalytic selective oxidation of aromatic compounds [1,2] and photocatalytic epoxidation of olefins [3,4]) receives increasing attention, since photocatalysis offers an alternative green route for the production of organics [5]. *p*-Phenylenediamine (PPD) is known as an important ingredient in the synthesis of many industrial chemicals, e.g., dyes [6], rubber antioxidants [7] and aramid textile fibers [8]. Generally, PPD is obtained by the catalytic hydrogenation of 4-nitroaniline (4-NA) under H_2 atmosphere [8]. However, this process suffers from the limitations of rigorous reaction conditions, high cost and tedious procedures.

Recently, the photoreduction of 4-NA to PPD by using photocatalysis in the presence of HCO_2^- or $\text{C}_2\text{O}_4^{2-}$ ions as hole scavengers has been reported [9–12]. This method provides a new feasible approach for the PPD production because it achieves the one-pot preparation of PPD in water *via* utilizing sunlight. Furthermore, this reaction has been systematically studied in our previous work [11,12]. Carbon dioxide radical ($\cdot\text{CO}_2^-$) is detected in the above system. This species has strong reductive ability ($\cdot\text{CO}_2^-/\text{CO}_2$, -1.80 V vs. RHE [11–13]), and therefore can reduce 4-NA to PPD in water

(4-NA/PPD, -0.30 V vs. RHE [14]). In order to further understand the photoreduction of 4-NA to PPD, we focus on searching new active species which are suitable for the photoreduction of 4-NA and clarifying their formation processes.

In previous work, alcohol radicals ($\cdot\text{R}'\text{OH}$, $\text{R}'=\text{CH}_2$, C_2H_4 and *i*- C_3H_6) have been reported to show strong reductive abilities (from -0.54 to -0.69 V vs. RHE) [15–17]. And some researchers have noticed the potential applications of these radicals in photoreduction reactions [18,19]. However, the roles of these radicals in the photoreduction reaction are still unclear. It is not clear whether these radicals are intermediate products or active species. Similarly, the clarification of their formation processes is also an interesting problem. It is not sure whether the alcohols react with photoinduced holes or hydroxyl radicals ($\cdot\text{OH}$) to give alcohol radicals. Furthermore, as far as we know, little attention has been paid to these species for the photocatalytic reduction of PPD.

Herein, the photocatalytic reduction of 4-NA to PPD *via* photocatalysis in the presence of different alcohols (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ and *i*- $\text{C}_3\text{H}_7\text{OH}$) was investigated in detail upon purging with N_2 . Electron spin resonance technique was introduced to detect the presence of these active species and to clarify their formation process in this system. Furthermore, on the basis of the experimental results, a mechanism was proposed to explain the photoreduction of 4-NA in the present alcohols. Our results may allow us to provide a new insight into the photoreduction of 4-NA to PPD by using photocatalysis in the presence of alcohols.

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2. Experimental

2.1. Photocatalytic reduction of 4-NA to PPD

For the photocatalytic reduction of 4-NA, an ozone-free 300 W Xe lamp (PLS-SXE300C, Perfectlight Co., Beijing, intensity: $\sim 1.35 \text{ W/cm}^2$ at $\lambda = 300 \text{ nm}$ and 0.96 W/cm^2 at $\lambda = 420 \text{ nm}$) with an infrared filter was used as the light source. Prior to the catalytic test, 80 mg of a photocatalyst (TiO_2 (Degussa Co.), ZnO (Aladdin Co.), $\text{PbBi}_2\text{Nb}_2\text{O}_9$ (self-made [11]) or CdS (Aladdin Co.)) was suspended in 80 mL of 4-NA (A.R., Alfa Aesar Co.) aqueous solution (20 mg/L) in a reactor (100 mL). After adding 0.2 mL of an alcohol (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$ or $i\text{-C}_3\text{H}_7\text{OH}$, A.R., Sinopharm Chemical Reagent Co.), the suspension was stirred in the dark for 30 min to ensure eliminate oxygen in the system by purging with nitrogen (>99.95%). As the reaction proceeded, 4 mL of the suspension was taken at a certain interval and was filtrated. The 4-NA and PPD concentrations during the reaction were analyzed by measuring the absorbance at 380 and 238 nm with a Cary 50 UV–vis spectrophotometer (Varian Co.), respectively. The whole photocatalytic process was carried out under N_2 bubbling with a flow rate of 60 mL/min.

2.2. Electron spin resonance

5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) spin-trapping electron spin resonance (ESR) spectra were recorded with a Bruker A300 spectrometer at room temperature. General instrument setting are as follows: microwave power, 6.35 mW; modulation amplitude, 3 G; receiver gain, 1×10^3 ; time constant, 10.24 ms; sweep time, 42 s; center field, 3507 G; sweep width, 80 G. The ESR signals were generated from a photocatalyst suspension (5 mg of the sample powders dispersed in 0.5 mL of ultrapure water) in the presence of 5 μL of alcohols and 15 mM DMPO (97%, J&K Co.) under band-gap irradiation. Prior to the experiment, the ultrapure water (resistivity, $16.5 \text{ M}\Omega \cdot \text{cm}$ at 25°C) was further purified by active carbon (2 mm & down, Alfa Aesar Co.).

3. Results and discussion

3.1. Photoreduction of 4-NA to PPD

Fig. 1a shows UV–vis spectral changes of the 4-NA aqueous solution over TiO_2 photocatalyst as a function of irradiation time in the presence of CH_3OH under UV light irradiation ($\lambda \geq 300 \text{ nm}$). A rapid decrease in the absorption of 4-NA at 380 nm along with simultaneous appearance of two peaks at 238 and 305 nm has been observed. The peaks observed at 238 and 305 nm are the characteristic peaks of PPD [10–12]. The results reveal that 4-NA can be reduced to PPD by TiO_2 photocatalyst in the presence of CH_3OH . The absorbance of PPD at 238 nm in the UV–vis spectrum is 1.25 after 25 min of UV light irradiation, while the 100% of 4-NA is converted. Therefore, the selectivity of PPD is $\sim 98\%$, since there is a liner relationship ($A = 0.0822 C - 0.0054$, $R^2 = 0.9994$) between the concentration (C) and the absorbance (A) at 238 nm for PPD [12]. Furthermore, GC–MS analysis results indicate that only PPD is detected after the reaction (see Figs. S1 and S2). These suggest that 4-NA can be efficiently reduced to PPD in the present system.

Control experiment (4-NA and CH_3OH without TiO_2 photocatalyst) exhibits negligible photocatalytic reduction of 4-NA (see Fig. S3a), which indicates the photolysis of 4-NA can be ignored under UV light irradiation. The photocatalytic activity of TiO_2 photocatalyst was also carried out under visible light irradiation ($\lambda \geq 420 \text{ nm}$). No significant reaction of 4-NA is observed (see Fig. S4). These results reveal that the reduction of 4-NA to PPD is attributed to the photocatalytic activity of TiO_2 photocatalyst.

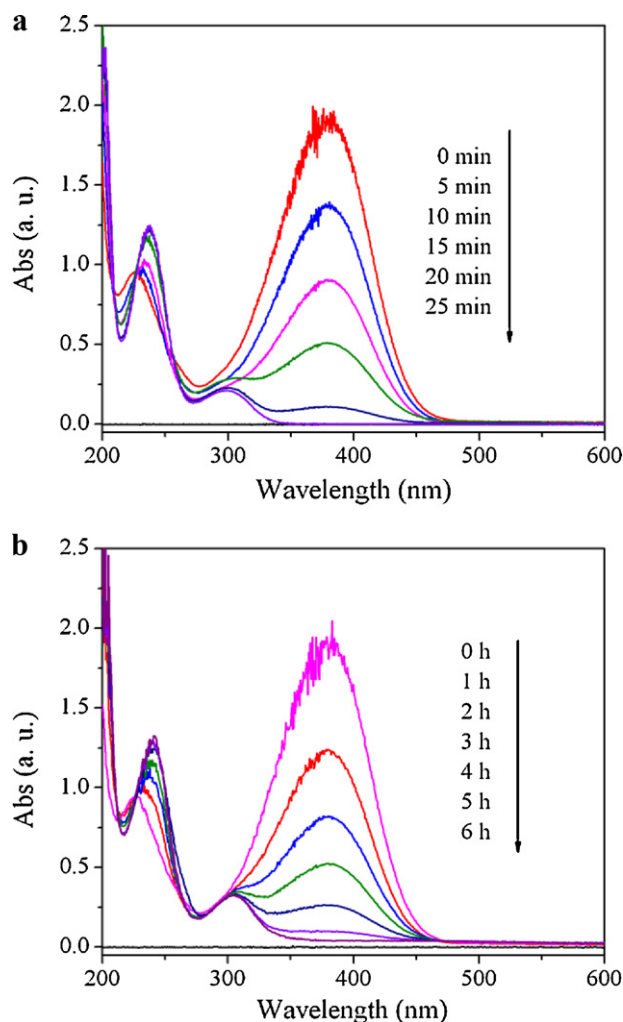


Fig. 1. UV–vis spectral changes of the 4-NA aqueous solution over (a) TiO_2 and (b) ZnO photocatalysts as a function of irradiation time in the presence of CH_3OH under UV light irradiation ($\lambda \geq 300 \text{ nm}$).

For comparison, the photoreduction of 4-NA over ZnO photocatalyst in the presence of CH_3OH was also investigated in this work. As shown in Fig. 1b, ZnO photocatalyst shows photocatalytic activity for the reduction of 4-NA to PPD, giving 100% of 4-NA conversion and 99% of PPD selectivity after 6 h of UV light irradiation. In our previous work, $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and CdS are active photocatalysts for the photoreduction of 4-NA in the presence of $\text{C}_2\text{O}_4^{2-}$ and HCO_2^- ions, respectively [11,12]. However, as shown in Fig. S5, no significant photoreduction of 4-NA is observed in the presence of CH_3OH under visible light irradiation ($\lambda \geq 420 \text{ nm}$) when $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and CdS are used as the photocatalysts.

3.2. ESR analysis

DMPO spin-trapping ESR technique has been introduced to investigate the photoreduction of 4-NA over different photocatalysts in the presence of CH_3OH . Fig. 2a shows DMPO spin-trapping ESR spectra of the samples aqueous suspensions under band gap irradiation ($\lambda \geq 300 \text{ nm}$ for TiO_2 and ZnO ; $\lambda \geq 420 \text{ nm}$ for $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and CdS). ESR signal of the DMPO- $\cdot\text{OH}$ adduct can be detected in the TiO_2 and ZnO aqueous suspensions under UV light irradiation ($\lambda \geq 300 \text{ nm}$). The formation of the $\cdot\text{OH}$ radicals can be attributed to the reaction between photoinduced holes (h^+) and H_2O molecules ($h^+ + \text{H}_2\text{O} \rightarrow \cdot\text{OH} + \text{H}^+$). However, $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and CdS cannot produce $\cdot\text{OH}$ radicals due to the

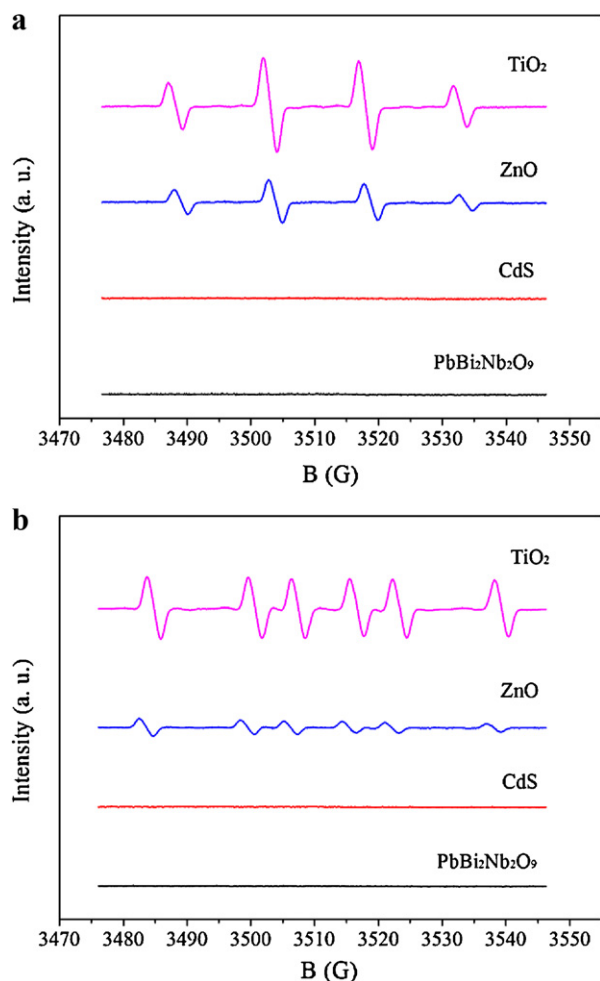


Fig. 2. DMPO spin-trapping ESR spectra of different photocatalysts aqueous suspension under band gap irradiation: (a) in the absence of CH_3OH and (b) in the presence of CH_3OH .

low redox potentials of valence bands (VB) for $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and CdS ($E_{\text{VB}}(\text{PbBi}_2\text{Nb}_2\text{O}_9) = 2.30 \text{ V}$ [11], $E_{\text{VB}}(\text{CdS}) = 1.90 \text{ V}$ [20] and $E(^{\bullet}\text{OH}/\text{H}_2\text{O}) = 2.72 \text{ V}$ [21] vs. RHE).

When CH_3OH is introduced into the presence system, sextet characteristic peaks of the $\text{DMPO}^{\bullet}\text{CH}_2\text{OH}$ adduct are clearly observed in the ESR spectra for TiO_2 and ZnO (Fig. 2b) [22]. It has been reported that the reduction potential of methanol radical ($^{\bullet}\text{CH}_2\text{OH}$) is -0.54 V vs. RHE [15]. Therefore, the species can reduce 4-NA to PPD ($E(4\text{-NA}/\text{PPD}) = -0.30 \text{ V}$ vs. RHE [14]). This can explain that TiO_2 and ZnO show photocatalytic activities for the reduction of 4-NA to PPD in the presence of CH_3OH , whereas $\text{PbBi}_2\text{Nb}_2\text{O}_9$ and CdS do not. Moreover, the signal intensity of the $\text{DMPO}^{\bullet}\text{CH}_2\text{OH}$ adduct in the ESR spectra for TiO_2 is stronger than that of ZnO . As a result, TiO_2 photocatalyst shows higher photocatalytic activity than ZnO photocatalyst for the reduction of 4-NA in the presence of CH_3OH (see Fig. 1).

In this work, similar phenomena were observed in the photoreduction of 4-NA over TiO_2 and ZnO photocatalysts due to their similar energy band structures. However, TiO_2 shows higher photocatalytic activity than ZnO for the reduction of 4-NA to PPD. For the sake of simplicity, further work for the photoreduction of 4-NA to PPD was mainly carried out over TiO_2 photocatalyst.

3.3. Formation of $^{\bullet}\text{CH}_2\text{OH}$ radical

As shown in Fig. 2, illuminated TiO_2 and ZnO photocatalysts can produce $^{\bullet}\text{OH}$ radicals, and therefore can give $^{\bullet}\text{CH}_2\text{OH}$ radicals. This

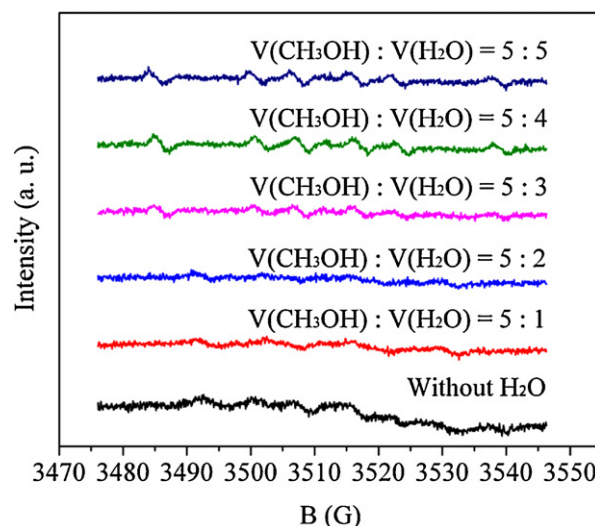
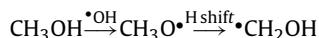


Fig. 3. DMPO spin-trapping ESR spectra of the TiO_2 aqueous suspension in the presence of CH_3OH and H_2O with different volume ratios under UV light irradiation ($\lambda \geq 300 \text{ nm}$).

may suggest that $^{\bullet}\text{OH}$ radicals rather than photoinduced holes of photocatalysts react with CH_3OH to give $^{\bullet}\text{CH}_2\text{OH}$ radicals. In order to confirm the formation process of the $^{\bullet}\text{CH}_2\text{OH}$ radical, DMPO spin-trapping ESR spectra of TiO_2 photocatalyst suspension in the presence of CH_3OH and H_2O with different volume ratios under UV light irradiation have also been obtained in this work. Fig. 3 shows that sextet characteristic peaks of the $\text{DMPO}^{\bullet}\text{O}_2^-$ adduct are observed in the TiO_2 photocatalyst methanol suspension. This confirms that TiO_2 photocatalyst can produce photoinduced electrons under UV light irradiation. However, the absence of the $\text{DMPO}^{\bullet}\text{CH}_2\text{OH}$ adduct signals in the ESR spectra is also observed. The $\text{DMPO}^{\bullet}\text{CH}_2\text{OH}$ adduct ESR signals can be detected when H_2O is introduced into this system. As mentioned above, illuminated TiO_2 photocatalyst can react with H_2O to give $^{\bullet}\text{OH}$ radicals. The results confirm that $^{\bullet}\text{OH}$ radicals rather than photoinduced holes of TiO_2 photocatalyst react with CH_3OH molecules to produce $^{\bullet}\text{CH}_2\text{OH}$ radicals. The possible formation process of $^{\bullet}\text{CH}_2\text{OH}$ radical is shown as follows [22].



3.4. Effect of $^{\bullet}\text{CH}_2\text{OH}$ radical

Generally, photoinduced electrons of TiO_2 and ZnO photocatalysts have reductive abilities ($E_{\text{CB}}(\text{TiO}_2) = -0.20 \text{ V}$, $E_{\text{CB}}(\text{ZnO}) = -0.07 \text{ V}$ vs. RHE) [20,21]. However, the reduction potential of 4-NA to PPD is -0.30 V vs. RHE [14]. Therefore, the photoinduced electrons (e^-) of TiO_2 and ZnO photocatalysts cannot reduce 4-NA to PPD due to their low redox potential. They only can participate in the reduction of water ($e^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2$, $E(\text{H}_2\text{O}/\text{H}_2) = 0.00 \text{ V}$ vs. RHE [21]) because H_2 is detected in the present system. Compared with photoinduced electrons, $^{\bullet}\text{CH}_2\text{OH}$ radical has stronger ability, and therefore can reduce 4-NA to PPD. In order to confirm the effect of $^{\bullet}\text{CH}_2\text{OH}$ radical on the photoreduction of 4-NA to PPD, the photoreduction of 4-NA to PPD over TiO_2 photocatalyst has been carried out under different conditions. As shown in Fig. S6, no significant photoreduction of 4-NA is observed after 25 min of UV light irradiation neither in the presence of TiO_2 photocatalyst upon purging with N_2 , or in the presence of TiO_2 photocatalyst and CH_3OH . However, 4-NA is rapidly reduced to PPD in the presence of TiO_2 photocatalyst and CH_3OH upon purging with N_2 under UV light irradiation (Fig. 1a). Evidently, both the addition of CH_3OH and

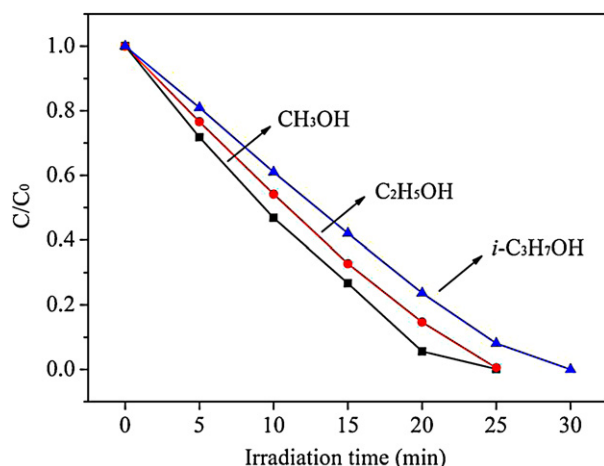


Fig. 4. Photoreduction efficiencies (C/C_0) of 4-NA as a function of irradiation time over the TiO_2 photocatalyst in the presence of different alcohols.

N_2 atmosphere are indispensable for the photocatalytic reduction of 4-NA over TiO_2 photocatalyst. N_2 atmosphere has been proved to be an important factor for the formation of the active species [11,12]. For the effect of CH_3OH , as mentioned above, TiO_2 photocatalyst can produce $\cdot\text{CH}_2\text{OH}$ radical in the presence of CH_3OH under UV light irradiation. The $\cdot\text{CH}_2\text{OH}$ radical has strong reductive ability. Therefore, this radical is an active species responsible for the photoreduction of 4-NA to PPD.

3.5. Effects of other alcohols

As mentioned above, TiO_2 and ZnO photocatalysts show the photocatalytic activities for the photoreduction of 4-NA to PPD under UV light irradiation in the presence of CH_3OH upon purging with N_2 . In this work, other alcohols ($\text{C}_2\text{H}_5\text{OH}$ and $i\text{-C}_3\text{H}_7\text{OH}$) have also been used to investigate the photoreduction of 4-NA. As shown in Figs. 4 and S3, 4-NA can be efficiently reduced to PPD over TiO_2 photocatalyst in the presence of $\text{C}_2\text{H}_5\text{OH}$ and $i\text{-C}_3\text{H}_7\text{OH}$ under UV light irradiation, giving 100% of 4-NA conversion and 98% of PPD selectivity. The total organic carbon values of the 4-NA aqueous solution before and after the photoreduction reaction have been measured by a total organic carbon analyzer (TOC-V CPH, Shimadzu Co.). The slight change of the total organic carbon value may be ascribed to the oxidation of alcohols by the TiO_2

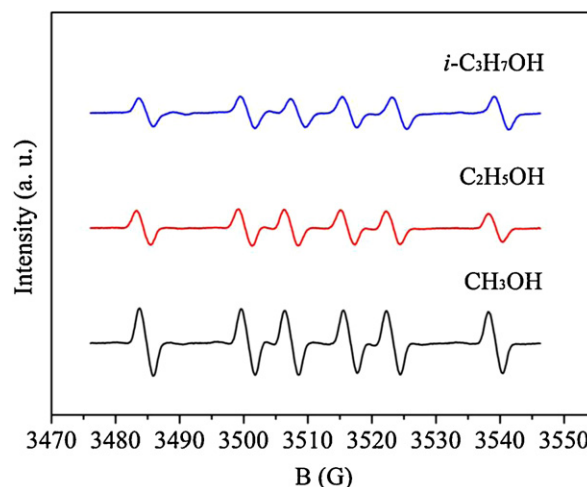


Fig. 5. DMPO spin-trapping ESR spectra of the TiO_2 photocatalyst aqueous suspension in the presence of different alcohols under UV light irradiation ($\lambda \geq 300 \text{ nm}$).

photocatalyst under UV light irradiation (see Table S1). Therefore, the photoreduction of 4-NA rather than the photooxidation of 4-NA is observed in the present system. Furthermore, ethanol ($\cdot\text{C}_2\text{H}_4\text{OH}$) and isopropanol ($\cdot i\text{-C}_3\text{H}_6\text{OH}$) radicals are detected by the DMPO spin-trapping ESR technique (Fig. 5). These alcohols radicals, like $\cdot\text{CH}_2\text{OH}$ radical, have strong reductive abilities ($\cdot\text{C}_2\text{H}_4\text{OH}$, -0.61 V vs. RHE; $\cdot i\text{-C}_3\text{H}_6\text{OH}$, -0.69 V vs. RHE) [16,17]. As a result, $\text{C}_2\text{H}_5\text{OH}$ and $i\text{-C}_3\text{H}_7\text{OH}$ are the efficient additives for the photocatalytic reduction of 4-NA to PPD. Moreover, the signal intensity of the DMPO- $\cdot\text{CH}_2\text{OH}$ adduct in the ESR spectra is stronger than that of the DMPO- $\cdot\text{C}_2\text{H}_4\text{OH}$ adduct or the DMPO- $\cdot i\text{-C}_3\text{H}_6\text{OH}$ adduct (see Fig. 5). Therefore, compared to other alcohols ($\text{C}_2\text{H}_5\text{OH}$ or $i\text{-C}_3\text{H}_7\text{OH}$), TiO_2 photocatalyst shows the highest photocatalytic activity for the reduction of 4-NA in the presence of CH_3OH (see Fig. 4).

3.6. Mechanism for the photoreduction of 4-NA

As a part of this work, the ^2H (D)-labeled experiments have been carried out to confirm the hydrogen atom source of PPD. Fig. S2b shows that the molecular ion peak of PPD is observed at $m/z = 108$ in the MS spectrum. However, when D_2O is used as the solvent, the MS spectrum gives an ion peak at $m/z = 110$ corresponding to

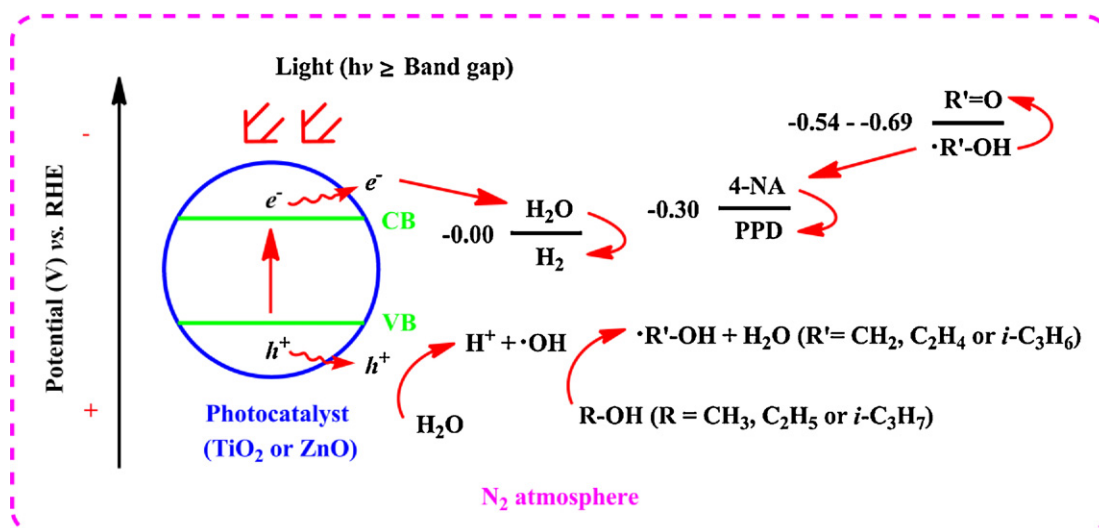
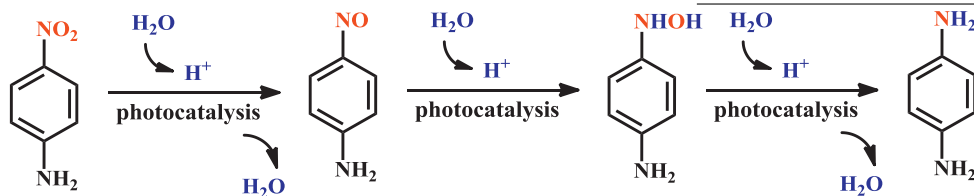


Fig. 6. Mechanism for the photocatalytic reduction of 4-NA to PPD via using photocatalysis.

the molecular ion peak of the D-atom-containing product [D]-PPD (see Fig. S7). The photoreduction of 4-NA to PPD was also investigated in the presence of CD₃OD. As shown in Fig. S8, there is no detection of [D]-PPD by the GC-MS analysis. The results indicate that the PPD formation is formed by the hydrogen transfer reaction between the 4-NA and H₂O molecules. Therefore, the main process of the photoreduction of 4-NA to PPD can be described as follows [11]:



On the basis of the above results, the mechanism for the photocatalytic reduction of 4-NA to PPD via using photocatalysis in the presence of alcohols (CH₃OH, C₂H₅OH and *i*-C₃H₇OH) is proposed as follows (see Fig. 6). When a photocatalyst (TiO₂ or ZnO) is illuminated under light ($h\nu \geq$ band gap), electron–hole pairs are created. Then, the photoinduced charge carriers migrate to the catalyst surface and participate in the redox reaction. Photoinduced holes react with water molecules to give \bullet OH radicals ($h^+ + \text{H}_2\text{O} \rightarrow \bullet\text{OH} + \text{H}^+$), while photoexcited electron directly participate in the reduction of water ($e^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2$) under N₂ atmosphere. The \bullet OH radicals will further react the alcohols to produce alcohol radicals ($\bullet\text{R}'\text{OH}$, R' = CH₂, C₂H₄ and *i*-C₃H₆). These radicals have strong reductive abilities ($E(\bullet\text{R}'\text{OH}/\text{R}'=\text{O}) = -0.54$ to -0.69 V vs. RHE), and hence can reduce 4-NA to PPD ($E(4\text{-NA}/\text{PPD}) = -0.30$ V vs. RHE).

4. Conclusions

Photoreduction of 4-NA to PPD over various photocatalysts (TiO₂, ZnO, PbBi₂Nb₂O₉ and CdS) was investigated in the presence of CH₃OH upon purging with N₂. DMPO spin-trapping ESR analysis results indicated that $\bullet\text{CH}_3\text{OH}$ radical was detected in the presence of TiO₂ and ZnO photocatalysts. Its formation was attributed to the reaction between the CH₃OH molecule and the \bullet OH radical. This radical had strong reductive ability. Therefore, TiO₂ and ZnO showed photocatalytic activities for the reduction of 4-NA in the presence of CH₃OH, whereas PbBi₂Nb₂O₉ and CdS did not. C₂H₅OH and *i*-C₃H₇OH were also found to be efficient additives for the photocatalytic reduction of 4-NA to PPD due to the presence of ethanol and isopropanol radicals. Furthermore, the results of the isotopic tracing method indicated that the PPD formation was formed by the hydrogen transfer reaction between the 4-NA and H₂O molecules. Our results could provide a new insight into the preparation of PPD by using photocatalysis in the presence of alcohols.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2012.10.025>.

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